

Desorption and Transformation of Nitroaromatic (TNT) and Nitramine (RDX and HMX) Explosive Residues on Detonated Pure Mineral Phases

Thomas A. Douglas · Marianne E. Walsh ·
Charles A. Weiss Jr · Christian J. McGrath ·
Thomas P. Trainor

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Abstract Explosive compounds, including known toxicants 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), are loaded to soils during military training. Their fate in soils is ultimately controlled by soil mineralogical and biogeochemical processes. We detonated pure mineral phases with Composition B, a mixture of

TNT and RDX, and investigated the fate of detonation residues in aqueous slurries constructed from the detonated minerals. The pure minerals included Ottawa sand (quartz and calcite), microcline feldspar, phlogopite mica, muscovite mica, vermiculite clay, beidellite (a representative of the smectite clay group), and nontronite clay. Energy-dispersive X-ray spectrometry, X-ray diffraction, and gas adsorption surface area measurements were made of the pristine and detonated minerals. Batch slurries of detonated minerals and deionized water were sampled for 141 days and TNT, RDX, and TNT transformation products were measured from the aqueous samples and from the mineral substrates at day 141. Detonated samples generally exhibited lower gas adsorption surface areas than pristine ones, likely from residue coating, shock-induced compaction, sintering, and/or partial fusion. TNT and RDX exhibited analyte loss in almost all batch solutions over time but loss was greater in vermiculite, beidellite, and phlogopite than in muscovite and quartz. This suggests common phyllosilicate mineral substrates could be used on military training ranges to minimize off-site migration of explosive residues. We present a conceptual model to represent the physical and chemical processes that occurred in our aqueous batches over time.

T. A. Douglas (✉)
U.S. Army Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory,
P.O. Box 35170, Fort Wainwright, AK 99703, USA
e-mail: thomas.a.douglas@usace.army.mil

M. E. Walsh
U.S. Army Engineer Research and Development Center,
Cold Regions Research and Engineering Laboratory,
72 Lyme Road,
Hanover, NH 03755, USA

C. A. Weiss Jr
U.S. Army Engineer Research and Development Center
Geotechnical and Structures Laboratory,
3909 Halls Ferry Road,
Vicksburg, MS 39180, USA

C. J. McGrath
U.S. Army Engineer Research and Development Center
Environmental Laboratory,
3909 Halls Ferry Road,
Vicksburg, MS 39180, USA

T. P. Trainor
Department of Chemistry, University of Alaska Fairbanks,
Fairbanks, AK 99775, USA

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1 Introduction

Artillery and mortar projectiles, hand grenades, and some small caliber ammunition contain explosive compounds 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). These toxic compounds (Rickert 1985) and their transformation products can be deposited to soils and eventually to surface water during training exercises. As a consequence, explosive residues on training range soils pose a long-term contamination risk for the Department of Defense and industry.

Nitramines like RDX and HMX are generally considered conservative in soils but nitroaromatic compounds (NACs) like TNT partition from aqueous solutions onto sediment surfaces, especially to clays (Haderlein et al. 1996; Brannon et al. 2002; Eriksson et al. 2004; Charles et al. 2006). TNT undergoes reductive transformation to 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) while RDX undergoes reductive transformation to hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) (Hawari et al. 2000). The uptake of explosive compounds and their transformation products onto mineral surfaces and the in situ transformation of munitions compounds is controlled largely by biogeochemical parameters (Braidia et al. 2002; Crocker et al. 2005; Dontsova et al. 2006; Larson et al. 2008; Douglas et al. 2009a, b; Hawari et al. 2000).

There is great potential in exploiting the surface chemical interactions between explosive residues and specific mineral phases as a means of sequestering or transforming explosive compounds to limit their off-site transport and minimize risk. There are numerous investigations of explosive sorption and transformation in the presence of mineral and soil surfaces (Yamamoto et al. 2004; Dontsova et al. 2006; Larson et al. 2008). Clays have shown the most promise in sorbing explosives and promoting the reductive transformation of NACs (Brannon et al. 2002; Haderlein et al. 1996; Hofstetter et al. 2003; Li et al. 2004; Charles et al. 2006; Roberts et al. 2006; Jaisi et al. 2007).

Much of the aforementioned research investigating the sorption/desorption and transformation of explosive compounds used the aqueous addition of

laboratory standards containing explosives to “load” the samples into soil and mineral batch reactors. This is despite the fact that explosive events load residues and not pure compounds to training range substrates and they load them heterogeneously (Hundal et al. 1997; Jenkins et al. 2006; Pantea et al. 2006; Douglas et al. 2011a). The chemical/physical pathways of explosive compounds in detonated (and subsequently wetted) impact area soils are initially controlled by the dissolution and desorption of compounds from the residues followed by sorption onto reactive surfaces. Results from aqueous addition studies may not fully represent the processes that occur on training ranges. To address this we detonated eight pure mineral phases with Composition B, a commonly used explosive formulation containing TNT, RDX, and HMX. We constructed batches by mixing detonated minerals with ultrapure water and monitored primary (TNT, RDX, and HMX) and transformation product (2ADNT, 4ADNT) concentrations for 141 days. Energy-dispersive X-ray spectrometry, X-ray diffraction, and surface area measurements were used to compare the pristine and detonated mineral surfaces and to determine if the extreme heat and/or pressures of detonation altered the mineralogical composition of the detonated substrates.

2 Experimental Section

2.1 Sample Detonation

Ten kilograms of eight pure minerals were procured from suppliers (Table 1). These included Ottawa sand (quartz and calcite), microcline feldspar, phlogopite mica, two muscovite micas, vermiculite clay, beidelite (a representative of the smectite clay group) and nontronite clay. An uli style knot of military detonation cord (cotton and asphalt tubing filled with pentaerythritol tetranitrate) was placed in the bottom of a paper cup containing 120 g of flaked Composition B. The paper cup was positioned at the bottom of a 20×40×50-cm steel can and samples containing 0.4 to 9 kg of each of the eight pure mineral types were gently poured into the steel can to a height of 15 cm. The steel can was located in a 2×2×2-m steel container that was open at the top. Sample detonation was initiated with a M21 shock tube initiator (lead, barium, antimony, and aluminum compounds with

Table 1 Mineralogical and chemical composition information for the pristine pure minerals investigated in this study

Sample	Mineralogy ^a	Organic matter (%) ^b	Cation exchange capacity (meq/100 g) ^b	pH ^b	Soluble salts (mmhos/cm) ^b	Bicarbonate (ppm) ^b	Mass in g/kg ^c							
							O	Na	Mg	Al	Si	K	Ca	Fe
Ottawa sand	Quartz, calcite, dolomite	0.1	1.0	7.3	0.1	3	62.3			0.1	37.6			
Microcline	Microcline, illite	0.2	1.6	8.3	0.1	6	54.8	0.5	0.0	6.7	25.3	9.2		3.4
Muscovite 1	Quartz, muscovite	1.7	1.2	5.8	0.1		51.7	0.5	0.4	17.0	19.3	8.0		3.1
Muscovite 2	Muscovite	2.6	0.9	6.0	0.1		51.2	0.4	0.5	16.2	18.9	8.5		4.4
Phlogopite	Phlogopite, calcite	0.1	2.9	9.7	0.1	5	46.0		14.6	4.9	17.3	8.5		8.8
Vermiculite	Vermiculite	1.7	2.6	9.8	0.1	3	49.7	0.5	13.1	9.3	15.5	5.5		6.3
Beidellite	Beidellite, quartz, calcite	1.2	55.5	9.8	2.2	9	59.8	1.5	2.0	9.3	21.9	0.2	1.7	3.7
Nontronite	Nontronite	0.1	41.3	6.8	0.9		34.9		0.2	0.4	4.2	20.8	1.6	37.9

The energy-dispersive X-ray spectrometry results from detonated samples were statistically significantly similar to the pristine samples but only data from the pristine samples is shown

^aBy X-ray diffraction

^bFrom a soil analysis done by Midwest Laboratories (Omaha, Nebraska). Organic matter percent was measured by chromic acid/oxidation/colorimetric methods; pH and soluble salts were measured in a 1:1 soil/water mixture by a combination electrode; cation exchange capacity was measured by the summation of cations and ammonium acetate saturation/displacement with NaCl distillation and titration

^cFrom energy-dispersive X-ray spectrometry. Three separate samples were analyzed individually and the mean values are presented here. Nickel and copper were not detected in any samples. Percent relative standard deviation values for each triplicate analysis were generally less than five

pentaerythritol tetranitrate and minor HMX) from a protected location 200-m away.

2.2 Chemical Composition, Mineralogy, Surface Imaging, and Surface Area Measurements of Pristine and Detonated Samples

The chemical composition (by mass) of major elements in the eight minerals was quantified using an energy-dispersive X-ray spectrometer (EDS; Quantax system, Bruker AXS, Ewing, NJ) on random powders using standard techniques. Based on numerous analyses of laboratory standards, the EDS yields a precision of $\pm 0.5\%$ by mass. Each sample was analyzed in triplicate.

The mineralogy of the pure mineral phases before and after detonation was determined by X-ray diffraction. We used a Philips PW1800 Automated Powder Diffractometer system (Philips International, Amsterdam, Netherlands) with $\text{CuK}\alpha$ radiation and step scanning from 2 to $65^\circ 2\theta$ with $0.05^\circ 2\theta$ steps. Collections lasted for 3 to 4 s per step. Diffraction patterns were collected using Datascan and analyzed using Jade (both from Materials Data Incorporated, Livermore, CA).

Brunauer–Emmett–Teller (BET) analysis was used to quantify the specific surface area of the mineral samples based on nitrogen adsorption (Brunauer et al. 1938). Multipoint surface area analyses were made from duplicate sample splits of approximately 2 g of each soil sample. Minerals were held under vacuum (0 torr) overnight at 105°C before surface area analysis with nitrogen gas (N_2) in a liquid nitrogen atmosphere (-194.8°C). Results from six relative pressure points were reduced to surface area values applying BET theory. Most samples were analyzed in triplicate and the mean values are given here.

2.3 Batch Experiment Aqueous and Mineralogical Samples

All sample batch slurries were prepared in duplicate. We mixed between 0.8 and 23.5 g of each sample into an amber glass bottle containing 480-mL of 18 M Ω water. The mass of detonated mineral used in each batch experiment was determined to ensure the maximum RDX and TNT concentrations in the aqueous phase (calculated by diluting the acetonitrile-extractable analyte mass in 480 mL of water) would be below the

solubility limits of 150 mg/L for TNT (Prak and O'Sullivan 2006) and 46.6 mg/L for RDX (Monteil-Rivera et al. 2004). The glass bottles were capped and placed on a platform shaker and shaken continuously at 200 rpm in the dark at 20°C for 3 months.

Ten 1-mL samples of the batch slurry solution were collected from the batches at the following elapsed times: 30 min and 3, 9, 17, 34, 52, 74, and 141 days. The 1-ml sample aliquots were pipetted into a 7-ml amber glass vial with a polytetrafluoroethylene (PTFE, Teflon) lid. Two milliliters of 18 M Ω water and 1 ml of HPLC-grade acetonitrile were added to each vial. Samples were stored at -20°C in the dark until they were analyzed. Concentrations of RDX, HMX, TNT, 2ADNT, 4ADNT, MNX, and DNX were determined following extraction and analytical methods in SW846 Method 8330B [U.S. EPA 2006]. Samples were filtered through a Millex-FH PTFE (Teflon) 0.45- μm filter and introduced with a 100-ml sample loop into a Finnigan SpectraSYSTEM Model P4000 liquid chromatography (Thermo Electron) using a ultraviolet/visible absorbance detector at 254 nm (cell path 1 cm). Separations were achieved on a 15 cm \times 3.9 mm (4 μm) NovaPak C8 column at 28°C and eluted with 1.4 ml/min of 15:85 isopropanol/water (v/v). A calibration standard (8095 Calibration Mix A at 10 mg/L in acetonitrile) was prepared from reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference material included the target analytes except MNX, DNX, and TNX that were obtained from Dr. Ronald J. Spanggard at the Stanford Research Institute (Menlo Park, CA). The percent relative standard deviation of the explosive compound measurements, based on numerous analyses of 100 ml of a laboratory spike solution, was less than 2% for the analytes measured.

Following the 141-day batch experiment the batch reactors were allowed to settle for 24 h and as much liquid as possible was decanted with a pipette. The remaining wetted mineral material was air-dried in a convection oven at 25°C until dried (48 h). A 10-mL aliquot of HPLC-grade acetonitrile was added to the dried samples to extract energetic residues (Sunahara et al. 1999; USEPA 2000; Walsh 2001). These samples, representing the acetonitrile-extractable explosive concentrations at the end of the batches, were placed on a platform shaker for 18 h at 200 rpm. One milliliter of the acetonitrile extract was mixed with 3 mL of 18 M Ω water and filtered

through a Millex-FH PTFE (Teflon) 0.45- μm filter. Concentrations of TNT, 2,4-DNT, HMX, RDX, 2ADNT, and 4ADNT from the soil extract solutions were determined following the procedures outlined above for aqueous samples.

3 Results and Discussion

3.1 Sample Detonation and Collection

Following detonation, a gray to black sooty sheen was evident on the surface of the samples (Fig. 1; Douglas et al. 2009a, 2011a; Jaramillo et al. 2011). Some material was shattered into smaller size fractions but clumped aggregates of samples were also present. Two sets of samples were collected from each of the detonation cans. The upper 0.5 cm of mineral

material was collected into high-density polyethylene bags using a precleaned polytetrafluoroethylene (Teflon) scoop. These samples were labeled “surface” and contained lightly aggregated particles coated with grayish soot. The remaining material, the “bulk” sample, was collected into a separate bag. We did not detect any undetonated Composition B particles in any of the samples through a $\times 10$ microscopic screening.

3.2 Chemical Composition, Mineralogy, and Surface Area Measurements of Pristine and Detonated Samples

Triplicate energy-dispersive X-ray spectrometry analyses of our pristine minerals are shown in Table 1. A comparison of pristine and detonated samples yielded statistically significantly similar elemental concentrations (analysis of variance with $\alpha=0.05$) which

Fig. 1 **a** undetonated Ottawa sand and **b** detonated Ottawa sand exhibiting the gray to black sooty sheen of detonation residues. **c** Undetonated vermiculite and **d** vermiculite following detonation. The *scale bar* numbered intervals are in centimeters

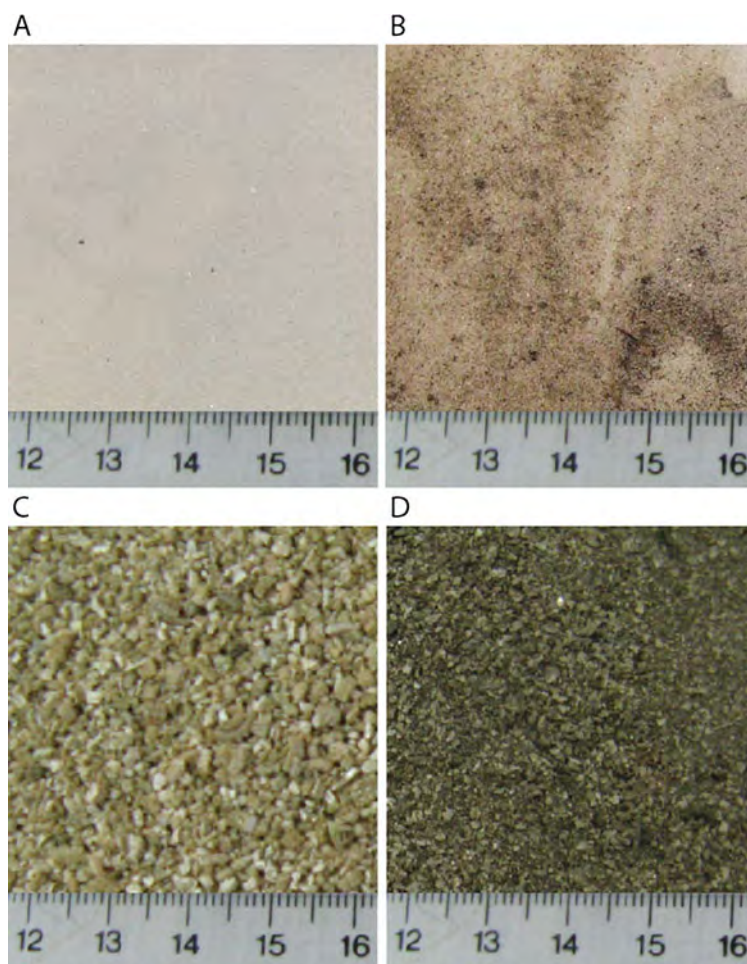


Table 2 Gas adsorption surface areas and detonation and explosive residue concentration information for the pure minerals investigated in this study

Name	Mass detonated (kg)	Sample type	Brunauer, Emmett, Teller gas adsorption surface area	Maximum expected aqueous concentration (mg/L) ^a			Apparent equilibrium aqueous concentration at day 141 (mg/L) ^b			TNT transformation product aqueous concentration at day 141 (mg/L)			Acetonitrile-extractable concentration at day 141 (mg/kg)		
				TNT	RDX	TNT	TNT	RDX	TNT	2ADNT	4ADNT	TNT	RDX	2ADNT	4ADNT
Ottawa Sand	4.99	Bulk 1	0.3	0.1	40.9	47.4	36.1	43.1	0.15	0.19	0.19	25.2	41.2	0.22	0.21
		Bulk 2			39.3	45.5	32.7	41.8	0.17	0.22	0.22	7.0	56.1	0.77	2.7
Microcline	3.18	Surface 1	1.3	0.9	29.8	42.3	15.0	23.7	0.08	0.11	0.11	336	1,456	ND ^d	ND
		Surface 2			30.4	43.1	15.8	23.6	0.08	0.13	0.13	444	2,585	ND	ND
Muscovite 1	0.73	Bulk 1			27.9	43.3	25.2	37.8	0.09	0.14	0.14	406	569	ND	1.4
		Bulk 2			27.7	43.0	31.2	35.2	0.09	0.11	0.11	632	2,721	ND	ND
Muscovite 2	1.82	Bulk 1	0.2	0.8	28.9	42.4	20.4	37.4	0.28	0.29	0.29	518	1,024	13.6	16.9
		Bulk 2			28.7	42.1	18.6	37.9	0.28	0.31	0.31	291	625	8.1	12.7
Phlogopite	2.27	Bulk 1	0.2	1.2	28.8	42.8	18.9	37.4	0.42	0.51	0.51	879	1,055	17	16
		Bulk 2			28.6	42.6	11.8	27.3	0.21	0.41	0.41	1,103	1,892	21	19
Vermiculite	0.36	Bulk 1	0.3	0.6	29.8	43.0	N/A	N/A	0.01	0.03	0.03	67.7	150	ND	ND
		Bulk 2			29.0	42.0	N/A	N/A	0.05	0.05	0.05	30.1	152	0.6	0.4
Beidellite	3.63	Bulk 1	7.9	5.2	5.5	21.0	N/A	N/A	0.15	0.28	0.28	DNM ^c	DNM	DNM	DNM
		Bulk 2			5.6	21.3	N/A	N/A	0.10	0.41	0.41	7.0	56.1	0.77	2.7
Nontronite	1.63	Surface 1	20.8	14.7	36.4	43.1	N/A	N/A	0.08	0.05	0.05	DNM	DNM	DNM	DNM
		Surface 2			36.4	43.2	N/A	N/A	0.06	0.09	0.09	55.2	21.3	0.6	0.4
		Bulk 1			35.5	44.2	N/A	N/A	0.03	0.03	0.03	94.0	2.7	0.6	0.5
		Bulk 2			34.3	42.7	N/A	N/A	0.05	0.07	0.07	188	12.8	1.0	0.9
		Surface 1	62.0	1.3	38.1	43.8	20.2	28.3	0.09	0.09	0.09	567	815	ND	ND
		Surface 2			38.5	44.3	38.5	46.7	0.07	0.07	0.07	1,108	2,049	ND	ND
		Bulk 1			39.0	43.5	19.5	24.4	0.03	0.05	0.05	DNM	DNM	DNM	DNM
		Bulk 2			38.2	42.6	21.3	28.3	0.04	0.05	0.05	1,376	1,762	ND	ND

Following Brunauer et al. (1938)

^a Calculated by multiplying the acetonitrile-extractable explosive compound concentration by the mass of sample and dividing by the amount of ultraclean water added^b Apparent equilibrium aqueous concentration values are the mean value of the final three measurements (days 52, 74, and 141) if these three consecutive values are within 10% of one another^c Did not measure this sample^d Was not detected in this sample

suggests the detonation process did not significantly alter the overall sample composition. The EDS results also confirm the high iron content of the nontronite clay compared to the other minerals.

A detailed comparison between the pristine and detonated X-ray diffraction patterns suggest that the structure of the low temperature minerals calcite and vermiculite were altered by detonation in some samples. The Ottawa sand samples include the minerals quartz, calcite, and dolomite. However, in some detonated Ottawa sand samples the highest intensity peak for calcite at $29^\circ 2\theta$ was almost completely absent in the diffraction patterns. In the vermiculite bulk samples the high intensity peaks at $7^\circ 2\theta$ and $27^\circ 2\theta$ are shifted by roughly $1^\circ 2\theta$ following detonation. These mineralogical changes are likely attributable to the intense heat ($2,400^\circ\text{C}$) and shock pressures (34 GPa) associated with Composition B detonation (Donnet et al. 1997; Keshavarz and Nazari 2006) and the relatively low temperature for calcite stability (melting temperature of 825°C) and vermiculite dehydroxilation (110°C ; Justo et al. 1993). None of the other samples exhibited changes in their X-ray diffraction patterns following detonation.

Results from BET measurements indicate detonation changes the gas adsorption surface areas of some samples (Table 2, Fig. 2). Vermiculite, nontronite, and beidellite gas adsorption surface areas were statistically significantly lower in the detonated samples than

in the pristine ones (analysis of variance with $\alpha=0.05$). Ottawa sand and microcline also had lower gas adsorption surface areas following detonation but the differences were not statistically different. Phlogopite, muscovite 1, and muscovite 2 saw increased gas adsorption surface areas following detonation but the values were not statistically different. The decreased gas adsorption surface areas following detonation in the vermiculite, nontronite, and beidellite sample pairs are likely caused by explosive residues, shock-induced compaction of the mineral grains, partial fusion from the intense heat of detonation, and/or sintering of grains (Douglas et al. 2011b).

3.3 Batch Experiment Aqueous and Mineralogical Samples

The explosive compound concentrations measured in the batches over time are presented in Figs. 3 and 4. The data points represent the mean (symbols) ± 1 standard deviation value for the two samples collected from duplicate batch reactors at each sample event. In general, the standard deviation values are within 15% of the concentration at a given sampling time. This suggests explosive residue loading to the batch substrates and the chemical and physical processes that control the explosive analyte concentrations over time are consistent and reproducible.

Fig. 2 The specific surface areas of our samples measured using Brunauer et al. (1938) theory. *Open symbols* denote pristine samples prior to denotation while *closed symbols* represent detonated samples. *Horizontal bars* denote the mean and *vertical lines* represent the standard deviation of the values ($N=3$)

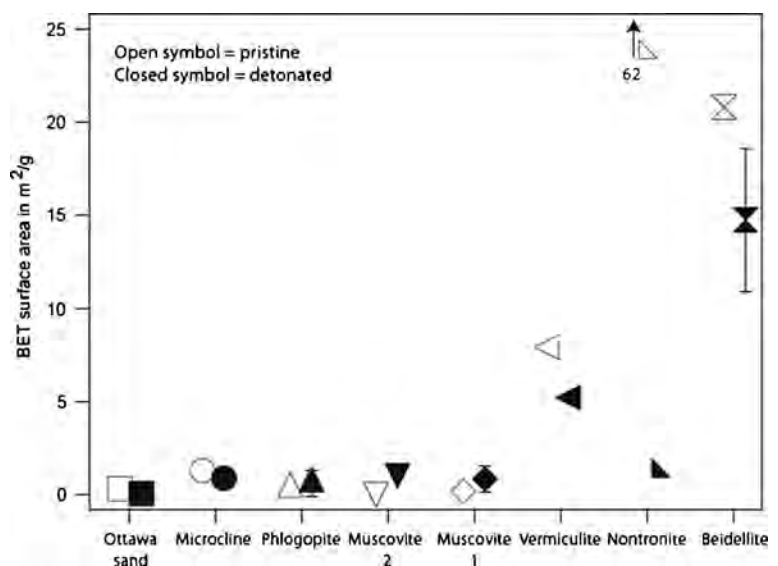
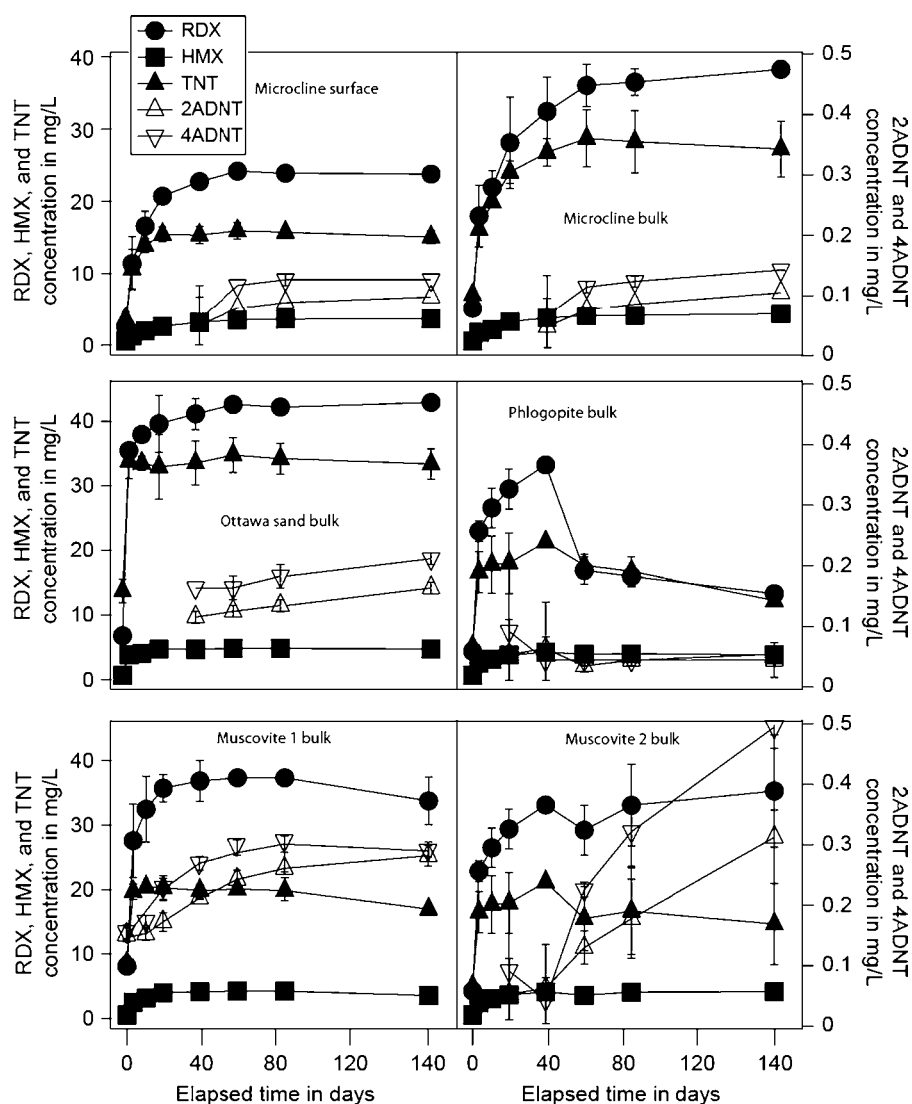


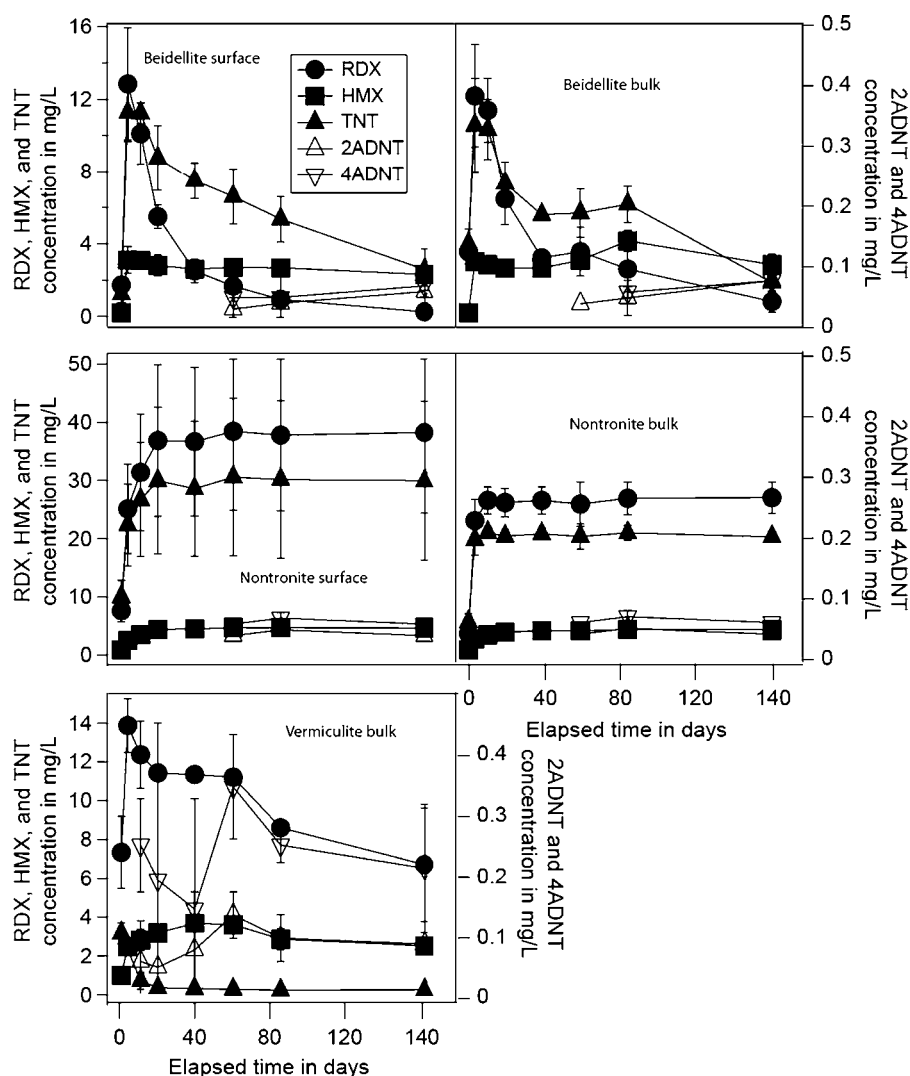
Fig. 3 Explosive compound concentrations measured from aqueous samples collected during the 141-day batch experiments for six of the pure minerals detonated in this study. The error bars denote ± 1 standard deviation of the values measured from the duplicate batches representing each mineral



TNT has been shown to readily sorb to soils (Pennington and Patrick 1999; Hundal et al. 1997; Brannon et al. 2002; Larson et al. 2008; Douglas et al. 2009b, 2011a), soil organic matter (Weissmahr et al. 1998; Eriksson et al. 2004), and clays (Weissmahr et al. 1997). Sorption is one way TNT could be lost from batch solutions over time. The reductive transformation of TNT to the monoamino-dinitro-toluenes 2ADNT and 4ADNT would also lead to a decrease in TNT aqueous concentrations. TNT reductive transformation is attributable to biotic and abiotic activity on the surfaces of soil and mineral substrates (Thorn and Kennedy 2002; Jenkins et al. 2006; Jaramillo et al. 2011; Douglas et al. 2011a, b).

The monoamines 2ADNT and 4ADNT were not present in our Composition B and were not detected in the acetonitrile-extracted samples of the minerals immediately following detonation. As such, their presence in the batch aqueous samples and the acetonitrile-extracted samples at the end of the batches (Table 2) can most likely be attributed to TNT transformation. 2ADNT and 4ADNT were generally not detected in the initial few batch aqueous samples (i.e., not within the first 9 to 17 days) but they were measured in all of the batches by day 52. 2ADNT and 4ADNT undergo transformation to monoamino and diamino metabolites (LaChance 2004) which we did not measure. As a consequence,

Fig. 4 Explosive compound concentrations measured from aqueous samples collected during the 141-day batch experiments for five of the pure minerals detonated in this study. The *error bars* denote ± 1 standard deviation of the values measured from the duplicate batches representing each mineral



we cannot discern the amount to which adsorption versus transformation control the 2ADNT and 4ADNT concentrations in the batch slurries.

In all of the aqueous batch samples, except for beidellite batches, the RDX concentrations are greater than TNT (Figs. 3 and 4). The Composition B we used has a TNT/RDX ratio of 39/60 with 1% wax (U.S. Army 1990; Jaramillo et al. 2011). The phlogopite, beidellite, and vermiculite batch aqueous TNT/RDX values initially yield this ratio but over time the two analytes are present in similar concentrations due to the dramatic loss of both analytes from solution over time. This loss of both analytes from solution could be attributable to adsorption onto the minerals and/or the transformation of both analytes.

In general, the batches begin with low aqueous explosive compound concentrations and exhibit steadily increasing values for the first four sample events representing the first 34 days. For all of the samples except phlogopite, vermiculite, and beidellite the values remain somewhat consistent to the end of the batches. These stable values represent batches for which dissolution, sorption, and transformation processes appear to have reached equilibrium. Table 2 includes the apparent equilibrium explosive concentrations calculated from the final three samples in these batches (Douglas et al. 2011a). In the phlogopite, vermiculite, and beidellite samples the TNT and RDX concentrations decrease steadily after the first few sample events. This is likely due to adsorption of

the explosives from solution onto the mineral surfaces and/or the transformation of these explosive analytes to other compounds.

Recent results from an investigation of explosive residues in aqueous batches of detonated soils (Douglas et al. 2011a) and metal oxides (Douglas et al. 2011b) have shown that RDX detonation residues undergo both sorption and transformation to MNX and DNX. We identified MNX and DNX in all of the Ottawa sand batches, in both the muscovite 1 and muscovite 2 batches from day 34 onward, and in vermiculite during the final two sample events. Their values stayed below 1 mg/L and the MNX concentrations were always roughly twice the DNX values. We did not detect MNX or DNX in any of the phlogopite, vermiculite, or beidellite aqueous samples. The nitroso MNX and DNX are transient intermediates in the transformation of RDX to formaldehyde, nitrous oxide gas, and ammonium so it is possible that they were present briefly but were transformed in the batches (Larese-Casanova and Scherer 2008; Boparai et al. 2010).

3.4 A Conceptual Model of the Fate of Nitramine and Nitroaromatic Compounds in Detonated Soils

Figure 5 presents a conceptual model synthesizing the physical and chemical processes developed from the results of this study and from three companion investigations (Douglas et al. 2011a, b; Jaramillo et al. 2011). At time 0, ultrapure water is added to the batch reactor and the initial explosive analyte concentration (C_0) is measured. At step 1, the solution chemistry is controlled by the dissolution of the explosive compound residues and undetonated explosive materials. Dissolution is governed by competing sorption/transformation processes. An apparent equilibrium or steady-state (step 2) between the dissolution and sorption/desorption processes is reached over time through a balance of: sorption onto mineral surfaces; dissolution/precipitation depending on the analyte solubility in water (i.e., if the system has reached saturation with respect to a stable solid phase); and dissolution of explosive compound residues and undetonated primary explosive material. For conservative compounds that do not transform or undergo sorption or for non-reactive substrates (like microcline and Ottawa sand) this may be maintained indefinitely. In the later period of stage 2, steady-state

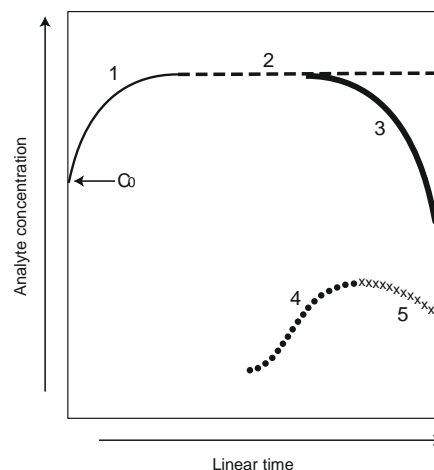


Fig. 5 A conceptual model of how desorption/sorption, dissolution, and transformation processes affect explosive compound concentrations in detonated minerals over time. The initial explosive concentration is measured immediately following the addition of ultrapure water (at time 0). (1) Dissolution of residues and undetonated explosive materials. (2) Apparent equilibrium for dissolution, sorption/desorption processes. For nontransforming compounds this may be maintained indefinitely. (3) Transformation leads to loss of primary explosive compounds from solution. (4) Transformation products begin to appear and reach equilibrium between sorption and transformation processes. (5) Transformation products transform and are lost from solution

concentrations of transformation products may be reached where the rates of formation and transformation are equal. For compounds like TNT that transform and/or sorb to mineral surfaces the primary explosive compounds are lost from solution in step 3 (i.e., phlogopite, beidellite, and vermiculite). In step 4 transformation products like 2ADNT and 4ADNT begin to appear (i.e., microcline, Ottawa sand, muscovite 1, and muscovite 2). These compounds either reach equilibrium or undergo transformation (step 5) and are lost from solution. Depletion of the explosive analytes is followed by a decrease in the concentration of transient transformation products.

4 Conclusions

Three important results emerge from this study illustrating how explosive detonation loads explosive residues to minerals in a manner markedly different than what is represented by aqueous addition. First, there are mineralogical changes to low temperature

minerals (calcite and vermiculite) following detonation that show soil mineralogies at impact areas may be altered by detonation events. Second, the mineralogical surface is altered by detonation. The three samples with the largest gas-exchangeable surface areas exhibited the largest decrease in gas-exchangeable surface area following detonation. The rest of the samples exhibited little change in gas-exchangeable surface area following detonation. Processes that could change the surfaces (and surface areas) of detonated minerals or soils include temperature or shock-induced melting, coating by residues, shattering of substrates, and sintering. Third, some mineralogies are associated with an enhanced loss of explosive compounds from solution and this is potentially caused by transformation and/or sorption. Phlogopite, beidellite, and vermiculite samples were associated with the greatest loss of TNT and RDX from aqueous solutions over time. These minerals are all phyllosilicates and some (such as beidellite and vermiculite) have swelling capabilities. Clearly the surface geochemical and physical interactions between explosive compounds and these three minerals warrant additional research.

The results from this and other studies suggest training and demolition ranges where explosives are commonly used could be designed using preferred soil characteristics or commonly available mineral substrates as amendments to enhance range sustainability. Applying reactive mineral substrates onto locations with high explosive residue concentrations could lower the environmental risk associated with training or demolition ranges by promoting the retention and/or transformation of explosive compounds.

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References

- Boparai, H. K., Comfort, S. D., Satapanajaru, T., Szecsody, J. E., Grossi, P. R., & Shea, P. J. (2010). Abiotic transformation of high explosives by freshly precipitated iron minerals in aqueous FeII solutions. *Chemosphere*, 79, 865–872.
- Braida, W. J., White, J. C., Zhao, D., Ferrandino, F. J., & Pignatello, J. J. (2002). Concentration-dependent kinetics of pollutant desorption from soils. *Environmental Toxicology and Chemistry*, 21(12), 2573–2580.
- Brannon, J. M., Price, C. B., Hayes, C., & Yost, S. L. (2002). Aquifer soil cation substitution and adsorption of TNT, RDX, and HMX. *Soil and Sediment Contamination*, 11(3), 327–338.
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2), 309–319.
- Charles, S., Teppen, B. J., Li, H., Laird, D. A., & Boyd, S. A. (2006). Exchangeable cation hydration properties strongly influence soil sorption of nitroaromatic components. *Soil Science Society of America Journal*, 70, 1470–1479.
- Crocker, F. H., Thompson, K. T., Szecsody, J. E., & Freckrickson, H. L. (2005). Biotic and abiotic degradation of CL-20 and RDX in soils. *Journal of Environmental Quality*, 34, 2208–2216.
- Donnet, J. B., Lemoigne, C., Wang, T. K., Peng, C. M., Samirant, M., & Eckhardt, A. (1997). Synthèse par explosive et par choc de nanodiamant. *Bull Société Chimiste France*, 134, 875–890.
- Dontsova, K. M., Yost, S. L., Simunek, J., Pennington, J. C., & Williford, C. (2006). Dissolution and transport of TNT, RDX, and composition B in saturated soil columns. *Journal of Environmental Quality*, 35, 2043–2054.
- Douglas, T. A., Walsh, M. E., McGrath, C. J., & Weiss, C. A. (2009a). Investigating the fate of nitroaromatic (TNT) and nitramine (RDX and HMX) explosives in fractured and weathered soils. *Journal of Environmental Quality*, 38(6), 1–10.
- Douglas, T. A., Johnson, L., Walsh, M. E., & Collins, C. (2009b). A time series investigation of the stability of nitramine and nitroaromatic explosives in surface water samples held at ambient temperature. *Chemosphere*, 76, 1–8.
- Douglas, T. A., Walsh, M. E., McGrath, C. J., Weiss, C. A., Jr. Jaramillo, A. M., & Trainor, T. P. (2011a). Desorption of nitramine (RDX and HMX) and nitroaromatic (TNT) explosive residues from soils detonated under controlled conditions. *Environmental Toxicology and Chemistry*, 30 (1–9). doi:10.1002/etc.383.
- Douglas, T. A., Walsh, M. E., McGrath, C. J., Weiss, C. A., Jaramillo, A. M., & Trainor, T. P. (2011b) The Fate of Nitroaromatic (TNT) and Nitramine (RDX and HMX) Explosive Residues in the Presence of Pure Metal Oxide Mineral Phases. In Chappell, M. A., Price, C. L., & George, R. D. (Eds.), *Environmental Chemistry of Explosives and Propellant Compounds in Soils and Marine Systems: Distributed Source Characterization and Remedial Technologies. ACS Symposium Series 1069, Chapter 11* (pp. 197–215). Washington, DC: American Chemical Society. doi:10.1021/bk-2011-1069.ch011.

- Eriksson, J., Frankki, S., Shchukarev, A., & Skyllberg, U. (2004). Binding of 2,4,6-Trinitrotoluene, Aniline and Nitrobenzene to dissolved and particulate soil organic matter. *Environmental Science and Technology*, 38, 3074–3080.
- Haderlein, S. B., Weissmahr, K. W., & Schwarzenbach, R. P. (1996). Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. *Environmental Science and Technology*, 30, 612–622.
- Hawari, J., Beaudet, S., Halasz, A., Thiboutot, S., & Ampleman, G. (2000). Microbial degradation of explosives: Biotransformation versus mineralization. *Applied Microbiology and Biotechnology*, 54, 605–618.
- Hofstetter, T. B., Schwarzenbach, R. P., & Haderlein, S. B. (2003). Reactivity of Fe(II) species associated with clay minerals. *Environmental Science and Technology*, 37, 519–528.
- Hundal, L. S., Shea, P. J., Comfort, S. D., Powers, W. L., & Singh, J. (1997). Long-term TNT sorption and bound residue formation in soil. *Journal of Environmental Quality*, 26, 896–904.
- Jaisi, D. P., Dong, H., & Liu, C. (2007). Influence of biogenic Fe(II) on the extent of microbial reduction of Fe(III) in clay mineral nontronite, illite and chlorite. *Geochimica et Cosmochimica Acta*, 71, 1145–1158.
- Jaramillo, A. M., Douglas, T. A., Walsh, M. E., & Trainor, T. A. (2011). Dissolution and sorption of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) and 2, 4, 6-trinitrotoluene (TNT) residues from detonated phyllosilicate mineral surfaces. *Chemosphere*. doi:10.1016/j.chemosphere.2011.04.066.
- Jenkins, T. F., Hewitt, A. D., Grant, C. L., Thiboutot, S., Ampleman, G., Walsh, M. E., Ranney, T. A., Ramsey, C. A., Palazzo, A. J., & Pennington, J. C. (2006). Identity and distribution of residues of energetic compounds at army live-fire training ranges. *Chemosphere*, 63, 1280–1290.
- Justo, A., Pérez-Rodríguez, J. L., & Sánchez-Soto, P. J. (1993). Thermal study of vermiculites and mica-vermiculite interstratifications. *Journal of Thermal Analysis*, 40, 59–65.
- Keshavarz, M. H., & Nazari, H. R. (2006). A simple method to assess detonation temperature without using any experimental data and computer code. *Journal of Hazardous Materials B*, 133, 129–134.
- LaChance. (2004). Toxicity and bioaccumulation of reduced TNT metabolites in the earthworm *Eisenia andrei* exposed to amended forest soil. *Chemosphere*, 55(1), 1339–1348.
- Larese-Casanova, P., & Scherer, M. M. (2008). Abiotic transformation of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) by green rusts. *Environmental Science and Technology*, 42(11), 3975–3981.
- Larson, S. L., Martin, W. A., Escalon, B. L., & Thompson, M. (2008). Dissolution, sorption, and kinetics involved in systems containing explosives, water and soil. *Environmental Science and Technology*, 42(3), 786–792.
- Li, H., Teppen, B. J., Johnston, C. T., & Boyd, S. A. (2004). Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. *Environmental Science and Technology*, 38, 5433–5442.
- Monteil-Rivera, F., Paquet, L., Deschamps, S., Balakrishnan, V. K., Beaulieu, C., & Hawari, J. (2004). Physico-chemical measurements of Cl-20 for environmental applications comparison with RDX and HMX. *Journal of Chromatography. A*, 1025, 125–132.
- Pantea, D., Brochu, S., Thiboutot, S., Ampleman, G., & Scholz, G. (2006). A morphological investigation of soot produced by the detonation of munitions. *Chemosphere*, 65(5), 821–831.
- Pennington, J. C., & Patrick, W. H., Jr. (1999). Adsorption and desorption of 2,4,6-trinitrotoluene by soils. *Journal of Environmental Quality*, 19, 559–567.
- Prak, D. J. L., & O'Sullivan, D. W. (2006). Solubility of 2,4-dinitrotoluene in seawater. *Journal of Chemical Engineering Data*, 51, 448–450.
- Rickert, D. E. E. (1985). *Toxicity of nitroaromatic compounds*. Washington, DC: Hemisphere.
- Roberts, M. G., Li, H., Teppen, B. J., & Boyd, S. A. (2006). Sorption of nitroaromatics by ammonium- and organic ammonium-exchanged smectite: Shifts from adsorption/complexation to a partition-dominated process. *Clays and Clay Minerals*, 54, 426–434.
- Sunahara, G. I., Dodard, S., Sarrazin, M., Paquet, L., Hawari, J., Greer, C. W., Ampleman, G., Thiboutot, S., & Renoux, A. Y. (1999). Ecotoxicological characterization of energetic substances using a soil extraction procedure. *Ecotoxicology and Environmental Safety*, 43(2), 138–148.
- Thorn, K. A., & Kennedy, K. R. (2002). ¹⁵N NMR investigation of the covalent binding of reduced TNT amines to soil humic acid, model compounds, and lignocellulose. *Environmental Science and Technology*, 36, 3787–3796.
- United States Army (1990). *Military Explosives*. Department of the Army, Headquarters, Washington, DC, Army Technical Manual TM 9-1300-214 (with Change No. 4).
- United States Environmental Protection Agency (USEPA). (2000). SW-846 EPA Method 8095: Explosives by gas chromatography. Test methods for evaluating solid waste. Office of Solid Waste, Washington, DC.
- United States Environmental Protection Agency (USEPA). (2006). SW846 Method 8330B Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC). USEPA Office of Solid Waste Standard Methods of Analysis Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Office of Solid Waste, Washington, DC.
- Walsh, M. E. (2001). Determination of nitroaromatic, nitramine, and nitrate ester explosives in soil by gas chromatography and an electron capture detector. *Talanta*, 54(3), 427–438.
- Weissmahr, K. W., Haderlein, S. B., & Schwarzenbach, R. P. (1997). In situ spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals. *Environmental Science and Technology*, 31, 240–247.
- Weissmahr, K. W., Haderlein, S. B., & Schwarzenbach, R. P. (1998). Complex formation of soil minerals with nitroaromatic explosives and other π -acceptors. *Soil Science Society of America Journal*, 62, 369–378.
- Yamamoto, H., Morley, M. C., Speitel, G. E., & Clausen, J. (2004). Fate and transport of high explosives in a sandy soil: Adsorption and desorption. *Soil and Sediment Contamination*, 13, 459–477.